U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-282 213

Identification and Distribution of Inorganic Components in Water What to Measure

Environmental Research Lab -Duluth, Minn

Sep 77

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/J-77-121	2. JOURNAL ARTICLE
3. RE PB 282 213	
4. TITLE AND SUBTITLE: Identification and Distribution of Inorganic Components in Water: What to Measure?	5. REPORT DATE
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Gary E. Glass	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: U.S. Environmental Protection Agency, Environmental Research Laboratory-Duluth, 6201 Congdon Boulevard, Duluth, Minnesota 55804	10. PROGRAM ELEMENT NO. 1BA608
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS: Same	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA-600/03

15. SUPPLEMENTARY NOTES: Reference: Glass, Gary E. 1977. Identification and Distribution of Inorganic Components in Water: What to Measure? Ann. N.Y. Acad. Sci. 298:31-46.

16. ABSTRACT

The chemical forms of inorganic components in water are widely varied and range from simple aquo complexes in solution to complicated silicate minerals in suspension. A variety of techniques are used to determine the total quantities of components in a particular aqueous environment by summation of the individual chemical species present. The biological response of organisms is not in general related to the total concentration of the components present but only to some fraction of the total, i.e., those chemical forms which interact most strongly with the biota and are absorbed. Chemical equilibria calculations are used to provide an estimate of the distribution of metal and ligand species in Lake Superior water and may be used to define important parameters of the system for study and measurement. Comparisons of calculated chemical species distribution with the direct toxic response of aquatic organisms show that only a small fraction of total copper is toxic while much larger fractions of the total are toxic for cadmium and mercury. When metals are bound in silicate minerals they do not exhibit direct toxic effects of fish but their internal organs do show metal uptake. Some inorganic components of Lake Superior have been identified and show concentrations in drinking water for lead, 0.1-150 µg/l; suspended solids, 0.5-39 mg/l; inorganic fibers, up to one billion cummingtonite-grunerite (amosite) and fiberglass, depending upon the time and place of sampling.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chemical complexes Inorganic components in water Chemical speciation Equilibria calculations Bioassay Lake Superior Biological impacts Uptake of particles by fish Toxicity of mercury, cadmium, copper, NTA, and EOTA Lead, asbestos, chlorine, fiberglass in drinking water	Aquatic pollutants and biological effects with emphasis on neoplasia REDEQL Equilibria modeling Lake Superior	07/B 06/T,F

18. DISTRIBUTION STATEMENT: RELEASE TO PUBLIC	19. SECURITY CLASS (This Report): UNCLASSIFIED	21. NO. OF PAGES: 18
	20. SECURITY CLASS (This page): UNCLASSIFIED	22. PRICE: A02-A01

REPRODUCED BY NATIONAL TECHNICAL INFORMATION SERVICE U. S. DEPARTMENT OF COMMERCE SPRINGFIELD, VA. 22161

EPA-600/J-77-121
JOURNAL ARTICLE

Reprinted from
ANNALS OF THE NEW YORK ACADEMY OF SCIENCES
Volume 298 Pages 31–46
September 29, 1977 25378

IDENTIFICATION AND DISTRIBUTION OF INORGANIC COMPONENTS IN WATER: WHAT TO MEASURE?

Gary E. Glass

Environmental Research Laboratory
United States Environmental Protection Agency
Duluth, Minnesota 55804

Inorganic components of water and food contribute to the nutritional requirements of living organisms. These components must be available in sufficient, but not excessive quantities, or toxicity may result. The importance of water versus food as a source of required quantities of metals has not been determined for man[1] or aquatic animals, but water is well recognized as a major source of toxic quantities for both. Of primary importance is the ability of organisms to accumulate needed components and to discriminate against excessive quantities or unneeded components in food and water. The molecular form of a component plays a major role in the mechanisms by which living membranes transport and discriminate among components.[2] It is generally thought that the most interactive form of a metal is the soluble aquo ion, that soluble complexes of most metals are less interactive, and that insoluble particulates are the least interactive. There are some important exceptions, however, such as soluble inorganic mercury complexes, cobalt complexed as cobalamin (vitamin B_{12}),[3] and inorganic fibers of asbestos[4] and glass.[5] The environmental factors that affect molecular forms of components, exposure of organisms, or the process of accumulation may have major biologic impacts.

Our ability to measure total concentrations of trace metals quantitatively has improved tremendously in the last five years, and it is now possible to measure the "background," or ambient, total concentrations of most metals in uncontaminated rivers and lakes.[6–8] The identification of inorganic contaminants in drinking water has been reported,[9–11] and national surveys are now being conducted to identify mineral fibers as well as "previously unidentified pollutants."[12,13] Our ability to measure molecular forms of the components of natural waters, however, is at best qualitative.[14] The basic problem remains unsolved, and research directed toward defining the aqueous molecular components present in different environments is increasing.[15] The driving force of this research is the need to determine the mechanisms by which environmental pollutants exert their adverse effects on man and aquatic animals. In the design of experiments to elucidate these mechanisms, one of the most difficult questions with regard to the components of natural water is to determine "what to measure." The intent of the discussion and data presented below is to give some insight into the complexity of environmental variables and, perhaps, to apply the findings to better determinations of and answers to this question.

Molecular Distribution of Inorganic Components in Water: Lake Superior Components as an Example

Analysis for the specific molecular forms of metals in natural waters has been reported only sparsely because of the lack of sensitivity and specificity of analytic techniques. The content of Lake Superior water for some components is well defined, and the data[6,8,16] are given in Table 1, along with components of somewhat uncertain

TABLE 1
MOLAR CONCENTRATIONS OF SOME COMPONENTS OF LAKE SUPERIOR WATER

Calcium	3.3×10^{-4}	Carbonate	8.7×10^{-4}
Magnesium	1.1×10^{-4}	Silicate	4.5×10^{-5}
Sodium	5.6×10^{-5}	Chloride	3.6×10^{-5}
Potassium	1.3×10^{-5}	Sulfate	3.6×10^{-5}
Strontium*	1.8×10^{-7}	Nitrate	1.6×10^{-5}
Barium*	1.0×10^{-7}	Hydroxide	6.3×10^{-7}
Iron*	5.4×10^{-8}	Carbon,* organic (mol wt as 5000)	6.0×10^{-7}
Copper	1.6×10^{-8}		
Zinc	1.1×10^{-8}	Phosphate	3.0×10^{-9}
Arsenic	1.1×10^{-8}	Hydrogen	1.6×10^{-8}
Manganese*	9.0×10^{-9}	Ammonia*	7.0×10^{-9}
Chromium*	4.0×10^{-9}		
Nickel*	3.0×10^{-9}		
Cobalt*	3.0×10^{-9}		
Selenium*	2.0×10^{-9}		
Lead	1.0×10^{-9}		
Cadmium	2.0×10^{-10}		
Silver*	1.0×10^{-10}		
Mercury*	5.0×10^{-11}		
Mercury, methyl*	5.0×10^{-12}		

*Indicated values are estimates.

total concentration. The detailed distributions in water of the molecular forms of each of these components are unknown, but the major inorganic components can be defined by considering the ligands present in natural waters and the chemical equilibria involved.[17–19] The assumption that natural waters are at chemical equilibrium is more nearly correct for reactions that are complete on a time scale of minutes or less than for reactions that have a time scale of years. By use of the concentrations of some of the components given in TABLE 1 and the chemical equilibria computer program REDEQL2,[18] and improved data base,[20] the first approximation of this distribution of 18 metals and 12 ligands has been made (TABLE 2). The concentrations given for the 288 aqueous species present are computed on the basis of the known information provided to the chemical equilibria model. The values given in parentheses are the numbers of different complexes that contain the metal and ligand and include mixed ligand complexes in some cases [i.e., ML(OH) and M(HL) (OH)]. Citrate is used as a representative ligand in place of organic carbon (fulvic acids, and so on) to provide a ligand with known stability constants and similar complexing characteristics, and ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA), and cysteine (CYST) are included to illustrate the distributions of trace quantities of organic ligands. The calculated distribution matches also, in general terms, what is known about the trace metal characteristics of the Lake Superior system. Copper is predominantly complexed with less than 1% present as the aquo ion,[21] cadmium is present mainly as the aquo ion,[7,22] and dissolved iron is completely complexed with organic ligands[17] in well-oxygenated systems at pH 7.8. The REDEQL2 program is also capable of considering oxidation-reduction reactions and precipitation and adsorption processes, and these phenomena will be considered at another time for the Lake Superior system.

For the stability constants used in the computations, the percentages of metals present as aquo ions are: Ca, 97; Mg, 97; Na, 100; K, 100; Sr, 100; Ba, 100; Zn, 60; Mn, 94; Ni, 37; Co, 55; Pb, 1; Cd, 56; Cu, 0.03; Ag, 96; and H_3CHg, 9 for Lake Superior water at pH 7.8. If the pH were 1 (0.1 M HCl), metal percentages in the form of

TABLE 2

CALCULATED DISTRIBUTION OF 18 METALS AND 12 LIGANDS IN LAKE SUPERIOR WATER*

	Ligand:	H_2O	OH	CO_3	Cl	SO_4	SiO_2	PO_4	NO_3	CIT	EDTA	NTA	CYST
	Total →	−1.74	−1.74	3.058	4.442	4.438	4.350	7.490	4.784	6.00	25.0	25.0	25.0
	↓	Free →	6.17	5.41	4.44	4.46	11.36	12.23	4.78	16.13	36.88	29.77	29.11
Metal		↓											
Ca	3.487	3.50	7.93	5.19(2)	†	5.82	†	9.18	†	6.08(3)	28.08(2)	25.29	†
Mg	3.959	3.97	7.40	5.63(2)	†	6.20	†	9.15	†	7.36(2)	32.06(2)	26.77	29.04
Na	4.252	4.25	†	8.55	†	8.11	†	†	†	†	38.50	31.74	†
K	4.889	4.89	†	†	†	8.34	†	†	†	†	†	†	†
Sr	6.75	6.75	11.58	†	†	†	†	12.74(2)	†	10.13	32.93(2)	29.84	†
Ba	7.0	7.00	12.03	†	†	†	†	†	†	26.78	33.98(2)	30.50	†
Fe(III)	7.268	18.61	9.30(3)	†	21.77(3)	19.20(2)	14.45	18.27	†	7.27(3)	26.80(3)	26.15(3)	43.52
Cu(II)	7.796	11.23	11.35(5)	10.09(4)	12.83(5)	13.56	†	15.51(2)	†	7.80(3)	27.22(3)	26.72(2)	†
Zn	7.959	8.18	9.38(5)	8.40(2)	11.22(5)	10.51	†	13.26	†	11.35	26.37(2)	25.78	26.45(2)
Mn(II)	8.26	8.29	10.62(2)	9.55	11.72(3)	10.61	†	12.97	†	11.07(2)	28.97(2)	29.08	32.86
Cr(III)	8.420	15.82	8.42(3)	†	19.58(2)	17.81	†	14.67	†	†	26.01(3)	†	†
Ni	8.47	8.90	9.83	8.91(2)	12.93(2)	11.22	†	14.27	†	9.13(3)	25.08(3)	25.79(2)	47.37
Co(II)	8.47	8.73	10.14(3)	8.84(2)	11.86(2)	10.85	†	14.01	†	26.11(2)	27.21(2)	26.32	27.80(2)
Pb	9.015	10.88	10.79	9.03	13.58	12.80	†	†	†	11.83	27.56	27.27	26.74
Cd	9.745	10.00	12.23(6)	10.12(2)	12.30(5)	12.32	†	18.56	14.17	11.57(3)	28.18(3)	28.09	†
Ag	10.0	10.02	14.22(2)	†	11.41(4)	13.47	†	†	†	19.39	38.62(2)	†	†
Hg	10.30	19.67	10.31(5)	13.94(2)	11.81(5)	21.90(2)	†	†	†	37.96	32.65(3)	33.01(2)	32.85
CHg	11.30	12.35	22.65(2)	†	11.34	†	†	†	†	†	†	†	25.45
Protonated ligand			−1.74	3.06(2)	†	10.13	4.35(2)	7.51	†	7.23(4)	33.46(3)	27.18(3)	25.22(3)

*Values are the negative logarithm of the concentration (moles/liter). Values in parentheses are numbers of different complexes that contain the ligand in the total metal-ligand concentration. CIT = citrate, a representative organic ligand in place of fulvic acids; EDTA = ethylenediaminetetraacetate; NTA = nitrilotriacetate; CYST = cysteine; CHg = methylmercuric ion; pH = 7.8.

†Stability of the constants are not in the data.

the aquo ion would be: Zn, 51; Mn, 69; Ni, 87; Co, 51; Pb, 27; Cd, 13; Cu, 37; Ag, 0.2; and H_3CHg, 0.005, with the remaining percentages as chloride complexes. These values are given for illustration and in most cases have not been verified with experimental measurements; they are useful, however, to point out the wide range of possibilities for the aquo form of metal in solution, which is generally thought to be the most biologically interactive, and the importance of making measurements of system-regulating parameters.

The most concentrated ligand components are present as calcium and magnesium complexes and as protonated forms. For trace concentrations of some ligands (EDTA, NTA, and cysteine), the most concentrated forms are NiEDTA, CaNTA, $H_3CHgCYST$, and HCYST. The distribution of trace ligands is strongly dependent on the extent to which the metals are complexed with the more abundant ligands, and in this particular calculation, Hg-CYST is a minor component of the trace cysteine ligand distribution. Even though the total concentration of mercury is 10 times that of H_3CHg, the aquo ion concentration, $Hg(H_2O)_6^{2+}$, is calculated to be 10^7 times less.

The analytic techniques that have been used to search for methyl metal compounds are not sensitive enough to detect methylmercury in the waters of the Great Lakes,[23] even though fish from some areas contain more than 0.5 ppm of mercury. Extrapolation of the tissue concentration of trout exposed to methylmercuric chloride at several concentrations for 38 weeks[24] gives an estimate of 0.001 μg/liter for "background" Lake Superior water, the value used in TABLE 1. An increasing number of this particularly interesting class of metal species present in natural waters has been reported recently. These forms of metals have remained in the spotlight since the discovery of methylmercury in fish. The methyl metals that have been reported are arsenic,[25] selenium,[26] lead,[27] tin,[28] and cobalt.[3] Future additions to these metals are expected, since the stable aqueous chemistry of thallium, indium, gallium, gold, platinum, and others in laboratory systems is known.[29]

The formation of inorganic aqueous complexes is well established, but only recently has direct quantitative chemical evidence for natural organic ligand-metal complexes been published.[30] There is also evidence for mixed complexes with more than one organic ligand, and stability constants for a few systems have been studied.[31] The formation of these mixed ligand-metal complexes has been discussed from a mechanistic point of view, and it is suggested that the large ligand molecules derived from humic substances may play a unique role by providing metals in complex form suitable for the highly stereospecific enzyme coordination sites.[32]

The importance of making key measurements can be seen from the results of the equilibrium solution model (TABLE 2). The characterization of the ligands present in natural water systems is important, because they can influence the metal reactivity of the system by controlling the concentrations of the reactive species. The hydrogen ion concentration plays a major role in determining the molecular species distribution of the ligands.

COMPARISONS OF DISTRIBUTION OF INORGANIC COMPONENTS IN WATER WITH EFFECTS ON AQUATIC ORGANISMS

The extent to which complexation of metals affects the toxicity to or accumulation in aquatic organisms has been studied for some inorganic and organic ligands.[33–35] The typical toxicity experiment designed to determine "safe levels" for aquatic animals[36] involves the additions of metals at ever-increasing concentrations until an adverse effect (primarily death, limited growth, and/or reproductive failure) is detected. An alternate approach is to keep the total metal concentration constant

and change some other environmental variable, such as pH,[37] or increase the amount of complexing ligand present until no adverse effects are noted.[38,39]

As a metal is added to water, the percentage distribution of metal complexes for that metal remains constant so long as the complexing ligands present are in excess. The metal percentage distributions change when a complexing ligand is added at concentrations roughly equivalent to the total concentrations of the metal (TABLE 3). For mercury, little change in metal distribution is calculated with added NTA at the concentrations given in TABLE 3. For systems that contain natural complexing ligands at the concentrations roughly equivalent to those of metals being added, the

TABLE 3

CALCULATED PERCENTAGE DISTRIBUTIONS OF COPPER, CADMIUM, AND MERCURY IN LAKE SUPERIOR WATER WITH ADDED CONCENTRATIONS OF NTA AND THE EFFECT ON *Daphnia magna**

	NTA:	10^{-25} M	5×10^{-7} M	10^{-6} M	2×10^{-6} M	5×10^{-6} M
Copper						
10^{-6} M	$Cu(H_2O)_6^{2+}$	0.62	0.062	0.025	0.011	0.0036
(63 μg/liter)	$CuCO_3$	8.3	0.83	0.35	0.14	0.049
	$Cu(CIT)^{2-}$	91	62	42	23	9.5
	$Cu(NTA)^-$	—	36	56	76	89
	$Cu(NTA)(OH)^{2-}$	—	0.66	1.0	1.4	1.6
	% survival	0	35	100	100	100
	number of young	0	6	101	219	214
Cadmium						
10^{-7} M	$Cd(H_2O)_6^{2+}$	56	13	6.8	3.4	1.3
(11 μg/liter)	$CdCO_3$	38	9.1	4.7	2.3	0.89
	$Cd(CO_3)(OH)^-$	3.9	0.93	0.48	0.23	0.091
	$Cd(HCIT)^-$	1.4	0.36	0.17	0.093	0.037
	$CdNTA^-$	—	76	87	93	98
	% survival	45	30	50	70	90
	number of young	0	4	68	137	107
Mercury						
10^{-7} M	$Hg(H_2O)_6^{2+}$	0.000†	0.000†	0.000†	0.000†	0.000†
(20 μg/liter)	$HgCl(OH)$	3.1	3.1	3.1	3.1	3.1
	$Hg(OH)_2$	96.9	96.9	96.9	96.8	96.7
	$Hg(NTA)(OH)^{2-}$	—	0.016	0.035	0.071	0.18
	% survival	0	0	0	0	0
	number of young	0	0	0	0	0
Lake Superior water, controls						
	% survival	90	100	95	100	95
	number of young	138	224	176	190	212

*Values for metal species are percentages. Citrate (10^{-6} M) is used to approximate the complexation by fulvic acids. NTA is nitrilotriacetate.

†0.000 is actually 0.000000042% as $Hg(H_2O)_6^{2+}$.

percentage distribution of complexes will change, and the fraction of the metal in a toxic form will change.

The sensitivity of *Daphnia magna* (water flea) to metals in solution can be used to demonstrate changing toxicity as a function of ligand concentration,[39] with total concentration of the metal held constant. The small differences in concentrations of

TABLE 4

CALCULATED PERCENTAGE DISTRIBUTIONS OF MERCURY IN LAKE SUPERIOR WATER WITH ADDED CONCENTRATIONS OF EDTA AND THE EFFECT ON *Daphnia magna**

EDTA:		10^{-25} M	3.4×10^{-7} M	3.4×10^{-6} M	1.7×10^{-5} M
Mercury distribution (%)					
$HgCl(OH)$		3.1	2.8	1.1	0.2
$Hg(OH)_2$		96.9	85.6	34.6	9.4
HgEDTA		—	11.6	64.2	90.4
Total mercury concentration					
5×10^{-11} M (0.01 μg/liter)	% survival	100	75	95	85
	number of young	272	242	259	53
	$Hg(H_2O)_6^{2+}$, 10^{-16} M†	0.021	0.019	0.008	0.002
1.3×10^{-8} M (2.6 μg/liter)	% survival	85	75	95	45
	number of young	159	350	225	144
	$Hg(H_2O)_6^{2+}$, 10^{-16} M	5.5	4.7	2.0	0.5
2.7×10^{-8} M (5.4 μg/liter)	% survival	35	45	20	35
	number of young	70	144	35	40
	$Hg(H_2O)_6^{2+}$, 10^{-16} M	12	10	4.2	1.1
5.7×10^{-8} M (11.4 μg/liter)	% survival	0	0	0	0
	number of young	0	0	0	0
	$Hg(H_2O)_6^{2+}$, 10^{-16} M	24	21	6.7	2.3

*Values for mercury species are percentages. EDTA is ethylenediaminetetraacetate.

†Calculated concentration of mercuric ion $[Hg(H_2O)_6^{2+}]$ is 0.021×10^{-16} M, where EDTA is 10^{-25} M.

ligand and the low toxic concentrations of total metal and calculated metal species distribution are seen for different solutions of copper, cadmium, and mercury, with varying concentrations of NTA in TABLE 3. The values in the Table for the percentage of metal complexed with the indicated ligand were computed by the same techniques indicated above. The bioassay techniques used were the same as those previously reported.[40] Twenty 1-day-old *Daphnia magna* were exposed to each of the metal and ligand combinations shown in TABLE 3. The solutions without added NTA indicate that 10^{-6} M copper, 10^{-7} M cadmium, and 10^{-7} M mercury concentrations exceed the LC_{50}. The numbers of young produced by the animals that survived the tests are given below the percentage of survival and are an additional measure of biologic sensitivity. The changing distribution of the molecular forms in solution as the concentration of NTA is increased in TABLE 3 compares with the observed biologic response. The fraction of the copper present as the aquo ion and carbonate changes more rapidly than that for cadmium, and the biologic response follows this trend. Even at the highest concentration of NTA, cadmium is exerting a toxic effect on reproduction as compared to the controls. Mercury is calculated to be completely complexed with chloride and hydroxide and shows no change in form or reduced toxicity as the concentration of NTA is increased.

TABLE 4 shows the calculated forms of mercury with EDTA, a stronger complexing ligand than NTA, chloride, or hydroxide. The toxicity indicated by the percentage of survival of the organisms that began the test and the number of young produced during the test shows no similar trend compared to copper or cadmium complexes. However, if cysteine, a sulfur-containing ligand, is present, the mercury is calculated to be complexed as $Hg(CYST)_2$, and the toxicity of mercury is reduced.

The uptake of mercury from solution by the gill tissue and blood of brook trout[37] shows little dependence on pH or calculated molecular form (TABLE 5) and indicates that, for this metal, the concentration of the total metal present is probably more important than that of the aquo ion, chloride, or hydroxy complexes.

One of the yet unanswered questions concerning metal uptake in aquatic organisms is whether particles can be directly incorporated into their bodies in a fashion similar to that of asbestos,[4] starch,[41] or polyvinyl chloride (PVC) particles[42] in man, and this question relates to the importance of this form of metals in the total water system. Fish have been proposed as sources of particulates found in human

TABLE 5

CALCULATED DISTRIBUTION OF MERCURY IN LAKE SUPERIOR WATER AT pH 6 AND 9 AND CONCENTRATIONS IN TISSUE OF FISH*

	pH 6.0	pH 9.0
Mercury distribution (M)		
$Hg(OH)Cl$	2.9×10^{-8}	9×10^{-11}
$Mg(OH)_2$	1.4×10^{-8}	4.5×10^{-8}
$HgCl_2$	2.4×10^{-7}	7×10^{-15}
$HgCl^+$	1×10^{-11}	3×10^{-17}
$HgOH^+$	9×10^{-12}	3×10^{-16}
$Hg(H_2O)_6^{2+}$	2×10^{-14}	8×10^{-20}
Mercury concentration in tissue* (μg/g)		
Gills	3.6	2.5
Red blood cells	2.2	2.3
Controls (both tissues)	0.2	0.2

*Yearling brook trout were exposed for 5 days to 4.5×10^{-8} M Hg (9 μg of Hg/liter) added as $HgCl_2$ to Lake Superior water at 9°C. From Drummond *et al.*[37]

TABLE 6

DISTRIBUTION OF METALS THAT ORIGINATE FROM NEUTRON-ACTIVATED IRON ORE MINE TAILINGS IN PARTICULATES, WATER, AND FISH TISSUE*

Radionuclide	Exposure* Time (days)	Solids and Water (pCi)	Water (pCi)	Tissue: Liver and Kidney† (pCi/fish)	Tissue: Liver and Kidney† (pCi/g)	Weight‡ of Tailings in Liver and Kidney (μg/fish)
^{47}Ca	4	5.4×10^4	3.8×10^4	~0.5	8	8.3
^{54}Mn	4	1.1×10^6	6.7×10^4	4.4	41	6.2
^{59}Fe	4	3.4×10^7	6.0×10^3	5.6	63	0.25
^{60}Co	4	6.3×10^5	1.2×10^4	0.6	7	1.4
^{86}Rb	4	$< 3.0 \times 10^5$	9.7×10^4	47	530	350
^{134}Cs	4	2.7×10^5	3.8×10^4	1.3	12	6.3
^{54}Mn	7	8.8×10^5	2.2×10^4	20	17	130
^{59}Fe	7	2.4×10^7	2.5×10^3	50	44	13
^{60}Co	7	4.0×10^5	9.4×10^3	2.2	1.8	32
^{86}Rb	7	$< 1.0 \times 10^5$	4.2×10^4	720	630	7100
^{134}Cs	7	2.9×10^5	1.8×10^4	4.8	4.1	88

*Exposure concentrations: 4 days, 150 mg/liter; 7 days, 600 mg/liter; rainbow trout fingerlings.
†Weight of these tissues averaged 2 g.
‡Based on the ratio of (picocuries in tissue/total picocuries in tailings) × (total grams of tailings).
§Assuming a particle size of $2 \times 0.2 \times 0.2\ \mu m^3$, this value would correspond to approximately 48×10^6 particles.

stomach tissue and are suspected to cause higher incidences of stomach cancer in fish-eating populations.[43] The exposure of brook trout to high concentrations of suspended minerals shows no acute toxicity, but the transfer of metals from the particles to water and fish tissue has been observed[44]; the data are presented in TABLE 6. The particles were iron ore mine tailings less than 5 μm in diameter, composed primarily of cummingtonite-grunerite (an amphibole mineral) and quartz and having the following mean chemical composition (percentages): Fe, 10; Si, 10; Mg, 4; Ca, 2; Mn, 0.8; Na, 7; K, 0.3; Al, 0.3; and P, 0.2. The mineralogy of these particles has been characterized previously.[45] The particles were washed with distilled water to remove any already soluble material, neutron activated, and suspended in Lake Superior water where fingerling rainbow trout were exposed. The activities of the various radionuclides are given in picocuries, and their distributions among solid, water, and fish tissue are shown for two different experiments of 4 and 7 days' duration.

The various mechanisms by which the radionuclides are transferred from solid to water, solid to fish, and water to fish are complex and, as the data in TABLE 7 indicate, are probably different for each element. The more "soluble" or exchangeable the element between solid and water, the more accumulation in the internal organisms of the fish. The "insoluble" elements, iron and cobalt, in the bioassay water showed the least amount of uptake. The last column in TABLE 7 shows the calculated mass of minerals based on the ratio of tissue activity to total solid activity for a particular radionuclide, assuming a mechanism by which direct uptake from solids to fish occurs. The values for the calculated tissue content based on this assumption differ by a factor of 1000 (4-day exposure) and by a factor of 500 (7-day exposure), depending on which element was used to make the calculation. The number of particles that corresponds to the calculated mass of silicate minerals when ^{59}Fe, a 7-day

TABLE 7

ANALYSIS OF LAKE SUPERIOR WATER AT INTAKES AND AT THE TAP

	Water Intakes		
	Present	Past*	Tap Water
Metals (μg/liter)			
Arsenic	0.7	83	
Cadmium	0.02	bdl†	0.02
Chromium	(0.2)‡	9	
Cobalt	(0.2)	bdl	
Iron	3	23	
Manganese	0.5	—	
Nickel	(0.2)	2	
Lead	0.2	7 & 20	0.2–150
Inorganic fibers (fibers/liter)			
Cummingtonite-grunerite (amosite)	$70–700 \times 10^6$		$70–700 \times 10^6$
Chrysotile	bdl		bdl
Glass	bdl		bdl–1000×10^6
Nonmetals (μg/liter)			
Fluoride (H_2SiF_6)	(200)		920
Ammonia (H_2NCl)	(1)		390
Chlorine ($ClNH_2$)	0		1000
pH	7.8		7.5

*From Kopp & Kroner.[9]
†Below detection limit.
‡Values in parentheses are estimates.

exposure, an average particle size of $2 \times 0.2 \times 0.2\ \mu m^3$, and density of $3.4\ g/cm^{-3}$ are used is about 48×10^6 particles per fish in the liver and kidney. This value estimates an upper limit for the number of particles, if present, and may be used as a guide for research currently under way to determine actual values.[46] This mechanism of uptake does not appear to be predominant and is probably only one of several mechanisms of metal uptake. The experiment is complicated by the mixture of particle sizes and compositions, by different rates of dissolution and component uptake (soluble and particulates) through the gill, and by ingestion[47] and component excretion.

Particulate matter in water contributes to the total metal content of the sample, but this contribution is small for most metals in Lake Superior water and for waters that have 10 mg or less of average suspended sediments per liter. The contributions from solids (10 mg/liter) to the total metal content of the Lake Superior water sample (in percentages) have been calculated[8] and are: As, 0.6; Cd, 2; Hg, 2; Cu, 4; Zn, 5; Cr, 6; Pb, 10; Mn, 100; and Fe, 150. These values indicate that for many natural waters, the fraction of the total metal contributed from average suspended sediments is small, except for iron and manganese.

Temporal and Locational Variations and Sources of Inorganic Components in Drinking Water: Detailed Example from Duluth, Minnesota

The monitoring surveys of the past have left important factors unstudied, primarily because of the usual limits, time and money, but also because of the methodology employed. Extreme temporal fluctuations of contaminants have been revealed by the *continuous* monitoring and observations of the water in western Lake Superior, which is heavily contaminated with mineral fibers (Figure 1). The factors responsible for these fluctuations are mainly of climatologic origin and have been discussed in detail by Cook *et al.*[11,48] From November to June, when the lake is isothermal, large increases in concentration of amphibole minerals and fibers are observed compared to the summer months. Because past monitoring surveys and studies[49] have been conducted during the summer season, the results cannot give a true picture and at best reveal only the "tip of the iceberg." For the Duluth water supply, the average amphibole fiber count, estimated by using amphibole mass averages, in the summer is about 70×10^6 per liter, the annual average is about 120×10^6 per liter, and during "turbid periods," this value ranges from 400 to 700×10^6 per liter.[48,49] The total mineral fiber counts are about twice these numbers. Correlations of fiber count and amphibole mineral mass show the latter to be a reliable indicator of amphibole fiber count in Duluth's drinking water,[48] probably because they both originate from the same discharge of the Reserve Mining Company, Silver Bay, Minnesota. The discharge of iron ore mine wastes (tailings) began in October 1955 with 6000 tons/day and increased through 1964 to 67,000 tons/day, the present discharge rate.[50] This discharge has covered the surficial sediments of western Lake Superior to various depths, so that the resuspension during storms gives rise to increasingly high concentrations in the water as the total amount of dumped tailings increases. The quantities of total suspended solids present include sediment input from rivers that do not contain amphibole minerals and do not correlate with amphibole mineral mass or fiber count.

The methodology employed for fiber counting in the first study[11] that reported the discovery of asbestos fibers in Duluth's drinking water underestimated the number of mineral fibers present. By use of improved procedures, Cook has been

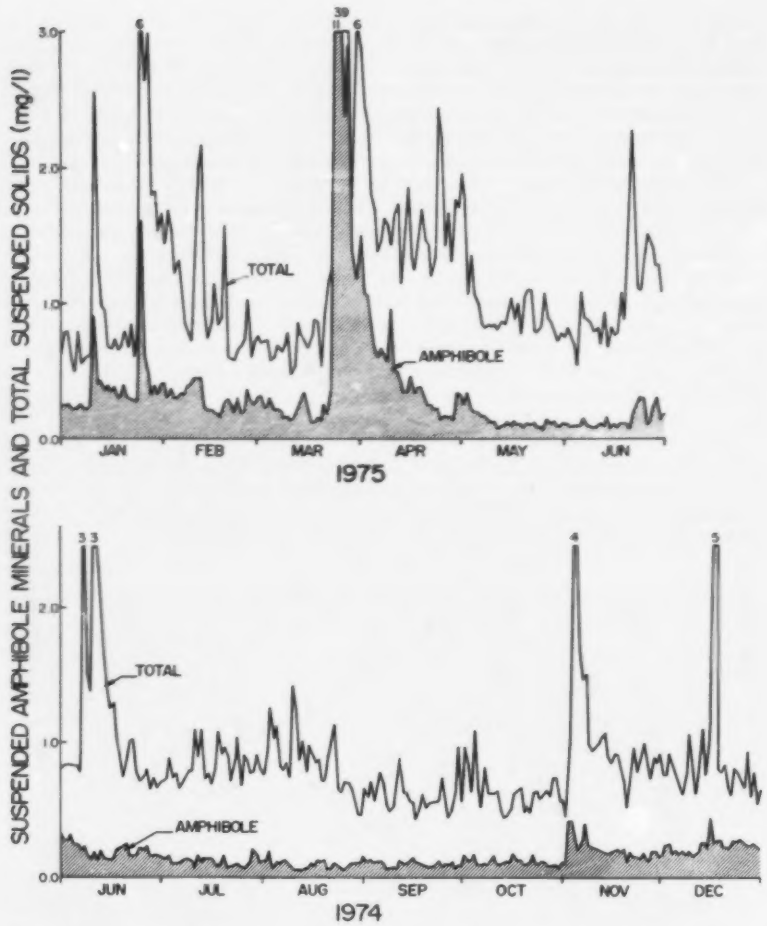

FIGURE 1. Temporal fluctuations of amphibole mineral mass and total suspended solids in the drinking water of Duluth, Minnesota at the Environmental Research Laboratory. From Cook *et al.*[48]

able to reproduce fiber counts to ±10% on five replicate samples and obtain agreement on samples shared with other laboratories.[48] Chrysotile, which has been reported previously in measurable quantities[49] in Duluth's drinking water, was probably the result of sample contamination and misidentification and has not been identified recently with improved techniques.

Duluth's water system has more than 325 miles of water mains and 20 reservoirs and towers of various sizes, which have a total capacity of about 72 million gallons, and pumps an average of 17 million gallons of water daily.[16] Some of the suspended

solids settle out in the mains and reservoirs of the municipal system. Measurable turbidity gradients exist within the system, especially during times of storms, when pulses of very turbid waters are pumped into the intake. During May and June, these sediments are resuspended by turbulence caused by the flushing of fire hydrants by the fire department. It is not uncommon to observe localized elevated turbidity within neighborhoods of up to 30 mg/liter for 2-3 days because of this practice. Amphibole mass and fiber concentrations are proportionately increased.

The high concentrations of asbestiform fibers are being reduced to some consumers by the use of cartridge filters and bottled water provided by the United States Army Corps of Engineers under court order in 1974. Membrane cartridge filters with fiberglass prefilters were installed in public buildings and restaurants. However, samples taken in November 1975 show that most of these filters failed because of high pressure gradients and water hammer and were leaking amphibole fibers and large quantities of fiberglass (FIGURE 2) into the filtered water. Monitoring the filtered water on a regular basis has reduced the problem, and replacing of membrane filter cartridges with those that do not have a fiberglass prefilter could eliminate it. The results of the filter testing program and methods of testing and analyses are being prepared for publication.[51]

The chemical analysis of Lake Superior water at Duluth for some inorganic components is given in TABLE 7. The values reported in the past[9] are quite different from the present values. The higher values for arsenic, chromium, lead, and iron may be caused by sample contamination during storage and shipment and by filtration or other methodologic or instrumental differences, because there has been no significant

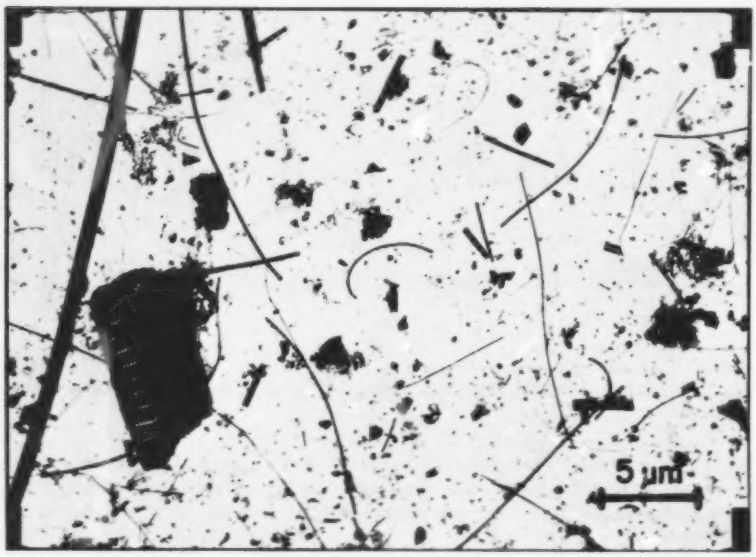

FIGURE 2. Electron micrograph of particles in drinking water from the second floor fountain at Lester Park Elementary School, November 11, 1975. Particles of fiberglass, diatoms, organic debris, and small amphibole fibers are present. The glass fiber content of this sample is estimated to be 550×10^6 fibers/liter.

pollution abatement since the time the earlier samples were taken and now. Extensive studies at the low concentrations of Lake Superior water by use of atomic absorption spectroscopy and anodic stripping voltametry show that contamination in the laboratory by lead and zinc and by cadmium in plastic sample bottles is most likely at these low concentrations.[7,52]

The elevated lead concentrations in tap water are caused by lead pipe connections from water mains to the user. Of the 25,900 water consumers in Duluth, 7000–8000 are connected with lead pipe that varies in length from about 10 to 100 m. The longer length gives lead concentrations of 150 μg/liter initially and falls to a steady-state concentration of 95 μg/liter with continuous flow. Some of these lead connections have been in place since 1899, and all were installed before 1940.

Chlorine has been added since 1911 to disinfect the lake water, and ammonia has been added since the mid-1920s to retain a chlorine residual throughout the Duluth system's 7-day flow-through time. The current chlorine dosage averages 1520 μg/liter, with a resultant residual that averages 1000 μg/liter. Fluoride is added by injecting a solution of hexafluorosilicic acid (H_2SiF_6) into the raw water intake and has been dosed in this fashion since April 2, 1970, as required by Minnesota state law. As a result of the additions of fluoride, ammonia, and chlorine, the pH is decreased about 0.3 of a unit from 7.8 to 7.5. The effects that these changes have had on the corrosion of pipes and the liberation of lead have not been studied, and it may be that the lake water itself is corrosive.

The examples given above show that important factors are often overlooked in surveys, and the epidemiologists who use analytic data from the literature must evaluate thoroughly all aspects of the methodology employed and have knowledge of the history, because it may be related to their studies.

Summary

The molecular form as opposed to the total quantity of inorganic components in water often determines the role that these components play in the aquatic environment. Although the metal aquo ion is generally thought to be *the* reactive form for biologic interactions, the fraction of the total metal present in this form may be small and highly variable, depending on the available complexing ligands and the magnitude of the interactions. Calculations by use of the chemical equilibria model and the inorganic components in Lake Superior water as an example show the distribution of metals and ligands water to be complex and indicate that analytic measurements must be sensitive in the range of 10^{-8}–10^{-12} M for most metals. Solutions that contain the same total metal concentration may be made completely nontoxic by adding complexing ligands. The comparison of calculated molecular distribution with effects on *D. magna* show that NTA and EDTA dominate the aquo chemistry of copper and cadmium, but not mercury. Mercury can be made nontoxic with cysteine.

Metals introduced to water in the form of silicate mineral particles show some transfer to water and fish tissue but on the basis of total metal measurement would contribute little total metal tissue content.

The analysis of drinking water from Duluth on a continuous basis for suspended contaminates and at different locations shows large fluctuations caused by a variety of factors. Asbestiform fiber and mass content vary over almost two orders of magnitude. Changes in time, processes, and materials over the years result in changes in the water supply. Lead, chlorine, ammonia, asbestiform fibers, hexafluorosilicic acid, and glass have been introduced to the drinking water at various times, locations, and concentrations. Studies designed to look at the overall result of these components must consider all of the sources and variations.

ACKNOWLEDGMENTS

The author thanks V. R. Magnuson, D. K. Harriss, J. E. Poldoski, P. M. Cook, J. H. Tucker, M. D. Lubratovich, and D. L. Peterson for providing information, B. J. Halligan, L. E. Anderson, and S. L. Forseth for assistance in the preparation of the manuscript, and W. A. Spoor for reviewing the manuscript.

REFERENCES

1. CRAUN, G. F. & L. J. MCCABE. 1975. Problems associated with metals in drinking water. J. Amer. Water Works Ass. **67**(11): 593–599.
2. PRESSMAN, B. C. & N. T. DEGUZMAN. 1975. Biological applications of ionophores: theory and practice. Ann. N.Y. Acad. Sci. **264:** 373–386.
3. LOWMAN, F. G. & R. Y. TING. 1973. The state of cobalt in seawater and its uptake by marine organisms and sediments. *In* Radioactive Contamination of the Marine Environment. Proceedings of the International Atomic Energy Agency Symposium. Series IAEA-SM-158/23. International Atomic Energy Agency. Vienna, Austria.
4. SELIKOFF, I.-J., E. C. HAMMOND & J. CHURG. 1972. Carcinogenicity of amosite asbestos. Arch. Environ. Health **25:** 183–186.
5. STANTON, M. F. & C. WRENCH. 1972. Mechanisms of mesothelioma induction with asbestos and fibrous glass. J. Nat. Cancer Inst. **48**(3): 797–821.
6. GLASS, G. E. & J. E. POLDOSKI. 1975. Interstitial water components and exchange across the water sediment interface of western Lake Superior. Verhandel. Int. Verein. Limnol. **19:** 405–420.
7. POLDOSKI, J. E. & G. E. GLASS. 1977. Considerations of trace element chemistry for streams in the Minnesota-Ontario border area. *In* Proceedings of the International Conference on Heavy Metals in the Environment. T. C. Hutchinson, Ed. Vol. II. Toronto, Ontario, Canada. In press.
8. POLDOSKI, J. E., E. N. LEONARD, J. T. FIANDT, G. F. OLSON, L. E. ANDERSON & G. E. GLASS. 1977. Occurrence of trace metal elements in nearshore waters from Lakes Huron and Superior. J. Great Lakes Res. Submitted for publication.
9. KOPP, J. F. & R. C. KRONER. 1967. Trace metals in waters of the United States. A five year summary of trace metals in rivers and lakes of the United States (Oct. 1, 1962–Sept. 30, 1967). NTIS Report PB 215680. United States Department of the Interior, Federal Water Pollution Control Administration, Division of Pollution Surveillance. Cincinnati, Ohio.
10. MCCABE, L. J., J. M. SYMONS, R. D. LEE & G. G. ROBECK. 1970. Survey of community water supply systems. J. Amer. Water Works. Ass. **62**(11): 670–687.
11. COOK, P. M., G. E. GLASS & J. H. TUCKER. 1974. Asbestiform amphibole minerals: detection and measurement of high concentrations in municipal water supplies. Science **185:** 853–855.
12. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. 1975. Preliminary assessment of suspected carcinogens in drinking water. Report to Congress. United States Environmental Protection Agency, Office of Toxic Substances. Washington, D.C.
13. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. 1976. Core activities of the Office of Toxic Substances (draft program plan). Report EPA 560/4-76-005. United States Environmental Protection Agency, Office of Toxic Substances. Washington, D.C.; DECARLO, V. 1976. Office of Toxic Substances, EPA Contract 68-01-3234.
14. STUMM, W. & H. BILINSKI. 1972. Trace metals in natural waters; difficulties of interpretation arising from our ignorance on their speciation. *In* Advances in Water Pollution Research—Trace Metals in Waters. S. H. Jenkins, Ed.: 39–52. Pergamon Press. New York, N.Y.
15. MINEAR, R. A., J. S. HENDERSON, C. L. MCENTYRE, R. R. ROSE, H. E. ALLEN & C.-M. SU. 1975. Nature and analysis of chemical species. Inorganics. J. Water Pollution Control Fed. **47**(6): 1118–1161.
16. CITY OF DULUTH, DEPARTMENT OF WATER AND GAS. 1975. Annual Report 1975. City of Duluth, Department of Water and Gas. Duluth, Minn.

17. STUMM, W. & J. J. MORGAN. 1970. Aquatic Chemistry. Interscience Publishers. New York, N.Y.
18. MOREL, F. & J. MORGAN. 1972. A numerical method for computing equilibria in aqueous chemical systems. Environ. Sci. Technol. **6**(1): 58–67.
19. LERMAN, A. & C. W. CHILDS. 1973. Metal-organic complexes in natural waters: control of distribution by thermodynamic, kinetic and physical factors. *In* Trace Metals and Metal-Organic Interactions in Natural Waters. P. C. Singer, Ed.: 201–235. Ann Arbor Science Publishers, Inc. Ann Arbor, Mich.
20. HARRISS, D. K. & V. R. MAGNUSON. 1976. Personal communication.
21. ANDREW, R. W. 1976. Toxicity relationships to copper forms in natural waters. *In* Toxicity to Biota of Metal Forms in Natural Water. R. W. Andrew, P. V. Hodson & D. E. Konasewich, Eds.: 127–143. International Joint Commission, Great Lakes Research Advisory Board. Windsor, Ontario, Canada.
22. GARDINER, J. 1974. The chemistry of cadmium in natural water—I—A study of cadmium complex formation using the cadmium specific-ion electrode. Water Res. **8**: 23–30.
23. CHAU, Y. K. & H. SAITOH. 1973. Determination of methyl mercury in lake water. Int. J. Environ. Anal. Chem. **3**: 133–139.
24. MCKIM, J. M., G. F. OLSON, G. W. HOLCOMBE & E. P. HUNT. 1976. Long-term effects of methylmercuric chloride on three generations of brook trout (*Salvelinus fontinalis*): toxicity, accumulation, distribution, and elimination. J. Fisheries Res. Board Can. **33**(12): 2726–2739.
25. BRAMAN, R. S. & C. C. FOREBACK. 1973. Methylated forms of arsenic in the environment. Science **182**: 1247–1249.
26. CHAU, Y. K., P. T. S. WONG, B. A. SILVERBERG, P. L. LUXON & G. A. BENGERT. 1976. Methylation of selenium in the aquatic environment. Science **192**: 1130–1131.
27. WONG, P. T. S., Y. K. CHAU & P. L. LUXON. 1975. Methylation of lead in the environment. Nature (London) **253**(5489): 263–264.
28. HUEY, C., F. E. BRINCKMAN, S. GRIM & W. P. IVERSON. 1974. The role of tin in bacterial methylation of mercury. *In* Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Ecosystems. Ottawa, Ontario, Canada.
29. WOOD, J. M. 1974. Biological cycles for toxic elements in the environment. Science **183**: 1049–1052.
30. MANTOURA, R. F. C. & J. P. RILEY. 1975. The use of gel filtration in the study of metal binding by humic acids and related compounds. Anal. Chim. Acta **78**: 193–200.
31. MANNING, P. G. & S. RAMAMOORTHY. 1973. Equilibrium studies of metal-ion complexes of interest to natural waters—VII—Mixed-ligand complexes of Cu(II) involving fulvic acid as primary ligand. J. Inorg. Nucl. Chem. **35**: 1577–1581.
32. LANGFORD, C. H. 1973. Mechanistic analysis of environmentally important mixed ligand complex formation; Ni^{2+} as an example. Inorg. Nucl. Chem. Lett. **9**: 679–688.
33. BROWN, V. M., T. L. SHAW & D. G. SHURBEN. 1974. Aspects of water quality and the toxicity of copper to rainbow trout. Water Res. **8**: 797–803.
34. PAGENKOPF, G. K., R. C. RUSSO & R. V. THURSTON. 1974. Effect of complexation on toxicity of copper to fishes. J. Fisheries Res. Board Can. **31**: 462–465.
35. LEE, G. F. 1973. Review paper—Chemical aspects of bioassay techniques for establishing water quality criteria. Water Res. **7**: 1525–1546.
36. EATON, J. G. 1973. Recent developments in the use of laboratory bioassays to determine "safe" levels of toxicants for fish. *In* Bioassay Techniques and Environmental Chemistry. G. E. Glass, Ed.: 107–115. Ann Arbor Science Publishers, Inc. Ann Arbor, Mich.
37. DRUMMOND, R. A., G. F. OLSON & A. R. BATTERMAN. 1974. Cough response and uptake of mercury by brook trout, *Salvelinus fontinalis*, exposed to mercuric compounds at different hydrogen-ion concentrations. Trans. Amer. Fisheries Soc. **103**(2): 244–249.
38. ANDREW, R. W., K. E. BIESINGER & G. E. GLASS. 1977. Effects of inorganic complexing on the toxicity of copper to *Daphnia magna*. Water Res. **11**: 309–315.
39. GLASS, G. E. & K. E. BIESINGER. 1977. Forms of copper, cadmium, and mercury in toxicity tests with *Daphnia magna*. In preparation.
40. BIESINGER, K. E. & G. M. CHRISTENSEN. 1972. Effects of various metals on survival, growth, reproduction, and metabolism of *Daphnia magna*. J. Fisheries Res. Board Can. **29**: 1691–1700.

41. VOLKHEIMER, G. 1974. Passage of particles through the wall of the gastrointestinal tract. Environ. Health Perspect. **9:** 215–225.
42. VOLKHEIMER, G. 1975. Hematogenous dissemination of ingested polyvinyl chloride particles. Ann. N.Y. Acad. Sci. **246:** 164–171.
43. HENDERSON, W. J., D. M. D. EVANS, J. D. DAVIES & K. GRIFFITHS. 1975. Analysis of particles in stomach tumours from Japanese males. Environ. Res. **9:** 240–249.
44. BRUNGS, W. A., G. E. GLASS & B. KAHN. 1976. Accumulation of radioisotopes by fish exposed to neutron-activated iron-ore mine tailings. Environ. Sci. Technol. Submitted for publication.
45. KRAMER, J. R. 1976. Fibrous cummingtonite in Lake Superior. Can. Mineralogist **14:** 91–98.
46. COOK, P. M. 1976. Personal communication.
47. ALLEE, W. C. & P. FRANK. 1948. Ingestion of colloidal material and water by goldfish. Physiol. Zool. **21:** 381–390.
48. COOK, P. M., I. B. RUBIN, C. J. MAGGIORE & W. J. NICHOLSON. 1976. X-ray diffraction and electron beam analysis of asbestiform minerals in Lake Superior waters. Annals 75CH1004-1 34-1: 1–9. The Institute of Electrical and Electronics Engineers, Inc. New York, N.Y.
49. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. 1975. Direct filtration of Lake Superior water for asbestiform fiber removal. Environmental Protection Technology Series EPA-670/2-75-050a-g. United States Environmental Protection Agency, National Environmental Research Center, Office of Research and Development. Cincinnati, Ohio.
50. VAPLON, G. G. & F. H. DICKSON. 1973. Tailings inventory—1972, Reserve Mining Company. Silver Bay, Minn.
51. COOK, P. M., G. E. GLASS & D. R. MARKLUND. 1977. An evaluation of cartridge filters for the removal of small fibers from drinking water. J. Water Pollution Control Fed. Submitted for publication.
52. POLDOSKI, J. E. & G. E. GLASS. 1976. Methodological considerations in western Lake Superior water-sediment exchange studies of some trace elements. *In* Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis. P. D. LaFleur, Ed. Vol. II: 1073–1088. National Bureau of Standards Special Publication 422. United States Government Printing Office. Washington, D.C.